



Standard Practice for Testing the Performance of Scanning Raman Spectrometers¹

This standard is issued under the fixed designation E1683; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—Units statement was inserted in Section 1.2 editorially in June 2014.

1. Scope

1.1 This practice covers routine testing of scanning Raman spectrometer performance and to assist in locating problems when performance has degraded. It is also intended as a guide for obtaining and reporting Raman spectra.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautions, see 7.2.1.

1.4 Because of the significant dangers associated with the use of lasers, ANSI Z136.1 should be followed in conjunction with this practice.

2. Referenced Documents

2.1 *ASTM Standards:*²

E131 Terminology Relating to Molecular Spectroscopy
E1840 Guide for Raman Shift Standards for Spectrometer Calibration

2.2 *ANSI Standard:*³

Z136.1 Safe Use of Lasers

3. Terminology

3.1 Terminology used in this practice conforms to the definitions in Terminology E131.

¹ This practice is under the jurisdiction of ASTM Committee E13 on Molecular Spectroscopy and Separation Science and is the direct responsibility of Subcommittee E13.08 on Raman Spectroscopy.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

4. Significance and Use

4.1 A scanning Raman spectrometer should be checked regularly to determine if its condition is adequate for routine measurements or if it has changed. This practice is designed to facilitate that determination and, if performance is unsatisfactory, to identify the part of the system that needs attention. These tests apply for single-, double-, or triplemonochromator scanning Raman instruments commercially available. They do not apply for multichannel or Fourier transform instruments, or for gated integrator systems requiring a pulsed laser source. Use of this practice is intended only for trained optical spectroscopists and should be used in conjunction with standard texts.

5. Apparatus

5.1 *Laser*—A monochromatic, continuous laser source, such as an argon, krypton, or helium-neon laser, is normally used for Raman measurements. The laser intensity should be measured at the sample with a power meter because optical components between the laser and sample reduce laser intensity. A filtering device should also be used to remove non-lasting plasma emission lines from the laser beam before they reach the sample. Plasma lines can seriously interfere with Raman measurements. Filtering devices include dispersive monochromators and interference filters.

5.2 *Sampling Optics*—Commercial instruments can be purchased with sampling optics to focus the laser beam onto a sample and to image the Raman scattering onto the monochromator entrance slit. Sample chamber adjustments are used to center the sample properly and align the Raman scattered light. A schematic view of a conventional 90° Raman scattering geometry is shown in Fig. 1. The laser beam propagates at a right angle to the direction in which scattered light is collected. It is focused on the sample at the same position as the monochromator entrance slit image. Other geometries such as 180° backscattering are also used. With single monochromators, a filter is normally placed in the optical collection path to block light at the laser frequency from entering the monochromator.

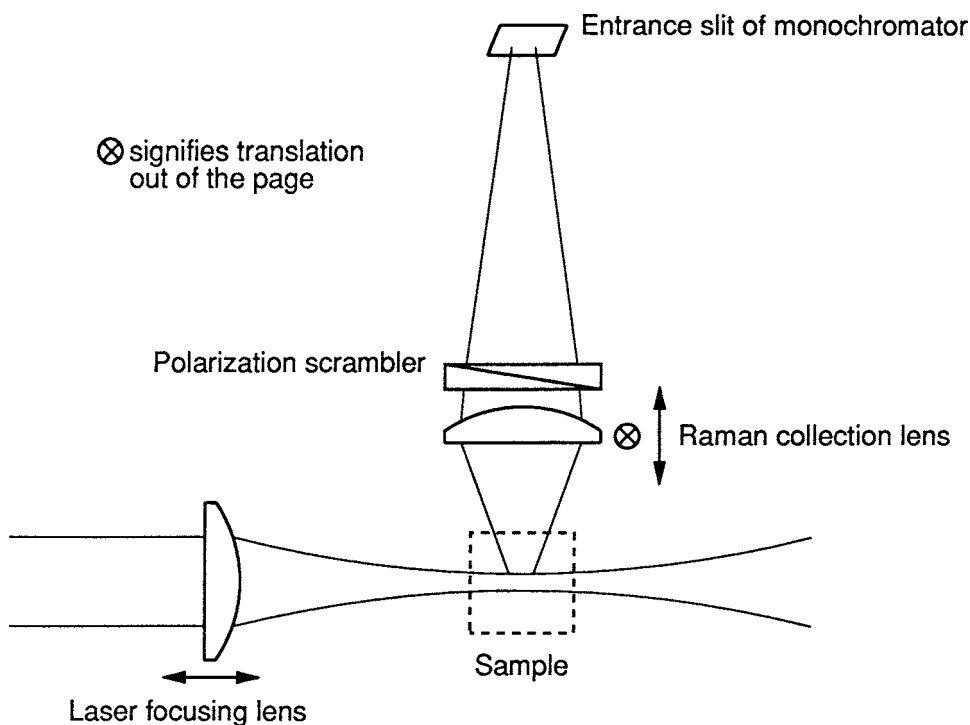


FIG. 1 Typical Raman Scattering Measurement Geometry

5.3 *Polarization*—For routine measurements the polarization of the laser at the sample is oriented normal to the plane of the page in Fig. 1. However, measurements using different polarizations are sometimes used to determine vibrational symmetries as part of molecular structure determinations. A variety of optical configurations can be used to make polarization measurements; a detailed discussion of these is beyond the scope of this practice. Briefly, for polarization simple measurements of randomly-oriented samples (most of the clear liquids), an analyzing element such as a polaroid filter or analyzing prism is added to the optical system and Raman spectra are collected for light scattered in (1) the same direction as the source (parallel), (2) perpendicular to the source. Depolarization ratios are calculated using Raman band intensities from the two spectra as follows:

$$\text{Depolarization ratio} = \frac{\text{Intensity parallel}}{\text{Intensity perpendicular}} \quad (1)$$

5.3.1 A polarization scrambler is shown in Fig. 1. This element is used to avoid making corrections for polarization-dependent grating effects. The scrambler is also frequently used during routine measurements and should be placed between the sample and entrance slit, close to the collection lens. A polaroid filter placed between the scrambler and collection lens provides a simple polarization measurement system.

5.4 *Monochromator*—A scanning monochromator used for Raman spectroscopy will exhibit high performance requirements. Double and triple monochromators have particularly stringent performance standards. During the original instrument design, features are usually introduced to minimize optical aberrations. However, proper maintenance of optical

alignment is essential. A focused image on the entrance slit should be optically transferred to and matched with the other slits. If the monochromator is not functioning properly contact the manufacturer for assistance.

5.5 *Photomultiplier Tube*—A photomultiplier can be used for detecting Raman scattered radiation. A tube with good response characteristics at and above the laser wavelength should be selected. Dark signal can be reduced with thermoelectric cooling for improved detection of weak signals. Current and voltage amplification or photon counting are commercially available options with photomultiplier tubes.

6. Guidelines for Obtaining and Reporting Raman Spectra

6.1 *Alignment of Optical Elements*—Refer to the manufacturer for detailed sample chamber alignment instructions. Upon installation, each optical component should be aligned individually. For optimal alignment the sample image should be centered on the entrance slit of the monochromator (often viewed through a periscope accessory or with the aid of a highly scattering sample or a white card at the slit). To perform the alignment a test sample is mounted in the sample compartment, centered in the laser beam, and translated to the approximate center of the monochromator optic axis. The monochromator is set to monitor a strong Raman band and its signal is maximized by adjusting the sample stage, lenses, or a combination of the two. Normally three orthogonal lens adjustments are used: (1) the laser focusing lens is translated along the direction of the beam; (2) the Raman scattering collection lens, positioned between the sample and the entrance slit, is translated along the direction of the propagating scattered light in order to provide focus; and (3) the collection lens

is translated perpendicular to the scattered light in order to scan the image of the laser-excited scattering volume across the width of the monochromator entrance slit. (Refer to Fig. 1.) This collection lens adjustment should be made during major instrument alignment (for example, during initial set-up), but should not be necessary during routine sample-to-sample alignment. Sample and lens adjustments should be repeated as necessary while the slits are narrowed from a relatively large initial width down to the size determined by the resolution requirements of the measurement.

6.2 Calibration:

6.2.1 *Spectral Response*—The spectral response of an optical spectrometric system will depend on the efficiency of the gratings (which is both wavelength and polarization dependent) and the spectral response of the photomultiplier tube. This can be measured routinely by collecting light from a tungsten halogen lamp or other NIST-traceable standard light source. A complete procedure for performing spectral response corrections has been published by Scherer and Kint (1).⁴ It is strongly recommended that corrections for spectral response be incorporated directly into the software when a computer is used to collect spectra.

6.2.2 *Wavenumber*—The accuracy of the wavenumber calibration over a large region should be determined using a standard low-pressure emission source with enough lines to make many measurements over the range of the instrument. Low-pressure mercury, argon, and neon lamps are frequently used. The non-lasing emission lines of the laser can also be used if the laser filtering device is removed. Accurate wavenumber values are available (2-9). For measurement at resolutions <0.5 wavenumbers a more rigorous calibration method should be employed.

6.3 *Recording Raman Spectra*—The following guidelines are provided for recording spectra with a rare meter and strip chart recorder or with a computer or digital signal averager. In both cases it is important to record a spectrum so that spectral features are not distorted by the mode of data acquisition.

6.3.1 *Recording With a Rate-Meter and Strip Chart Recorder*—The range on the rate-meter is set by monitoring the strongest peak in the spectrum. The relationship between the scan rate, spectral slit width, and time constant of the rate-meter, as recommended by IUPAC (10), is:

$$\frac{\text{Scan rate, (cm}^{-1}\text{/s)} \leq \text{spectral slit width, (cm}^{-1}\text{)}}{(4 \times \text{time constant (s)})} \quad (2)$$

In addition, the time constant of the recorder should be considerably faster than the rate-meter's time constant, and the speed of the paper should be adequate to measure the spectral features.

6.3.2 *Recording With a Computer or Signal Averager*—In this case one needs to define the increments in wavenumbers between data points. A minimum criterion is to collect five data points in the full width at half the maximum intensity (FWHM) of the narrowest spectral band. For example, if the slits were set to provide a measured band width at half maximum of 4 wavenumbers, then 1-wavenumber increments would produce five data points within the FWHM in a scan of a line from a plasma emission source. To better define peak shape decrease the size of the increments. This is especially important for bands that deviate from Lorentzian shape.

6.4 *Reporting Experimental Conditions*—The spectral slit width (wavenumbers), scan rate, laser wavelength and power at the sample, polarization conditions, integration time, corrections for instrumental response, type of spectrometer and detector, sample information (physical state, concentration, geometry, and so forth), and other important experimental conditions should always be recorded with the spectra and reproduced for performance testing. A complete record of the parameters to be specified is available in Table 1 of the IUPAC Recommendations for the Presentation of Raman Spectra in Data Collections (10).

7. Evaluation of Raman Instrument Parameters

7.1 The performance of an instrument should be evaluated regularly to determine if it has degraded. This is most easily accomplished with a test sample such as carbon tetrachloride measured under a set of standard conditions established for the

⁴ The boldface numbers in parentheses refer to a list of references at the end of the text.

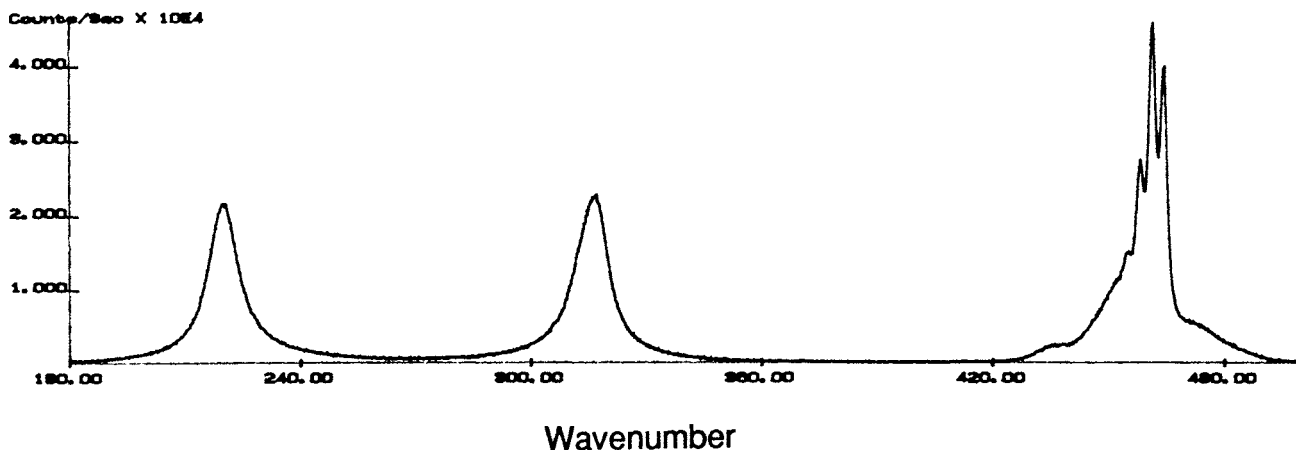


FIG. 2 Carbon Tetrachloride Raman Spectrum for Evaluating Resolution and Scanning Accuracy

TABLE 1 Recommended Frequencies from the Spectrum of Indene for Evaluating Scanning Accuracy

Band ^A	Frequency, cm ⁻¹
1	730.4 ± 0.5
2	1018.3 ± 0.5
3	1205.6 ± 0.5
4	1552.7 ± 0.5
5	1610.2 ± 0.5
6	2892.2 ± 1
7	3054.7 ± 1

^A Bands from Fig. 3.

particular instrument. Signal intensity and wavelength accuracy are the two spectral features to check. If peak signal levels have diminished or are shifted from accepted wavenumber values, the components of the system should be evaluated independently to locate the source of performance degradation. Guidelines for such an evaluation are as follows:

7.2 Test Samples—The following readily available materials are commonly used for evaluating the performance of Raman spectrometers:

7.2.1 Carbon Tetrachloride—The major Raman bands are 218, 314, and 459 cm⁻¹ (see Fig. 2). (**Warning**—Carbon tetrachloride is toxic and a suspected carcinogen. It is recommended that carbon tetrachloride be used in closed containers to avoid inhalation of harmful vapors.)

7.2.2 Cyclohexane—The major Raman bands are at 384.1, 801.3, 1444.4, and 2852.9 cm⁻¹.

7.2.3 Indene—There are many bands at well-known Raman Shift (2, 11, 12). Samples should be vacuum-distilled, sealed, and stored in the dark. A reference spectrum is shown in Fig. 3 (2).

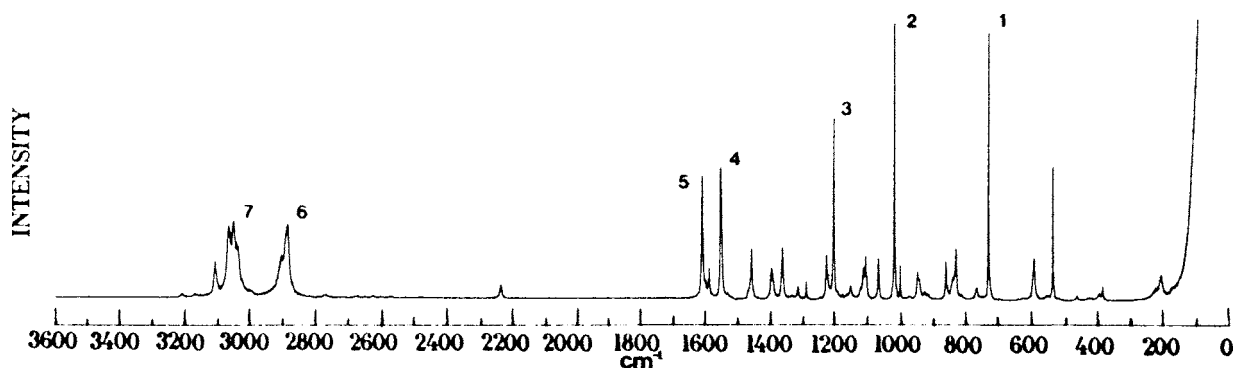
7.3 Monochromator—There is a trade-off between spectral resolution of a monochromator and the intensity throughput. The following five characteristics of a monochromator can be evaluated independently:

7.3.1 Spectral Bandwidth—The minimum spectral bandwidth that can be measured with a Raman spectrometer is determined by the focal length of the mirrors, the groove density of the gratings, and its optical alignment. Mirror focal length is determined during instrument design. Usually gratings with several groove densities are available from the manufacturer. The spectral bandwidth may be checked by

measuring the FWHM intensity of a sharp plasma line emitted from a low-pressure atomic source. The mercury line at 546.07 nm (1122.5 cm⁻¹ shift from the 514.53-nm argon ion laser line) is often used. If a lamp is not available the laser emission lines can be used. The spectral bandwidth of a double (additive) dispersing monochromator should ideally be one half that of a single monochromator with the same slits and grating. Most manufacturers specify bandwidths for their monochromators and measured values should be reasonably close to those specified (using the same slit widths and grating). For a double (additive) monochromator demonstrating an overly large bandwidth, each of the monochromator stages can be checked separately by closing its slits to a relatively narrow width (for example 50 μm), opening the slits of the other monochromator stage wider (for example, 300 μm), and measuring the emission line FWHM. The bandwidths of the individual stages should be the same and equal to twice the bandwidth of the combined stages. If one stage has a significantly larger bandpass than the other, and that bandpass is much larger than twice that expected for the entire monochromator, then it has a problem. Also, if combining the stages does not reduce the bandwidth as expected, then there is a problem and the manufacturer should be consulted.

7.3.2 Resolution—A test frequently used to check the resolution of Raman spectrometers is illustrated in Fig. 4. The four components of the mercury 579.1-nm emission line are distinctly visible. Alternately, the components of the carbon tetrachloride 459 cm⁻¹ Raman scattering band can be used, as shown in Fig. 2. The spectral bandwidth described in 7.3.1 is also commonly used as a convenient means to check resolution.

7.3.3 Coupling—If the stages of a Raman spectrometer are improperly coupled it may possibly go undetected in a resolution test. Poor coupling results in a loss in Raman signal intensity, often as a function of wavelength. To check the coupling of two monochromator stages, measure the Raman scattering of a test liquid at a major band intensity maximum. Set the entrance slit of the first stage and the exit slit of the second stage to narrow widths (for example, 50 μm). Set the intermediate slit(s) wider (for example, 150 μm) and record the Raman intensity. Then close the intermediate slit(s) to normal operating width (usually 20 % larger than the entrance slit, 60 μm for the example given). The intensity reduction should be



NOTE 1—Numbered band frequencies are identified in Table 1 for evaluating scanning accuracy.

FIG. 3 Indene Raman Spectrum

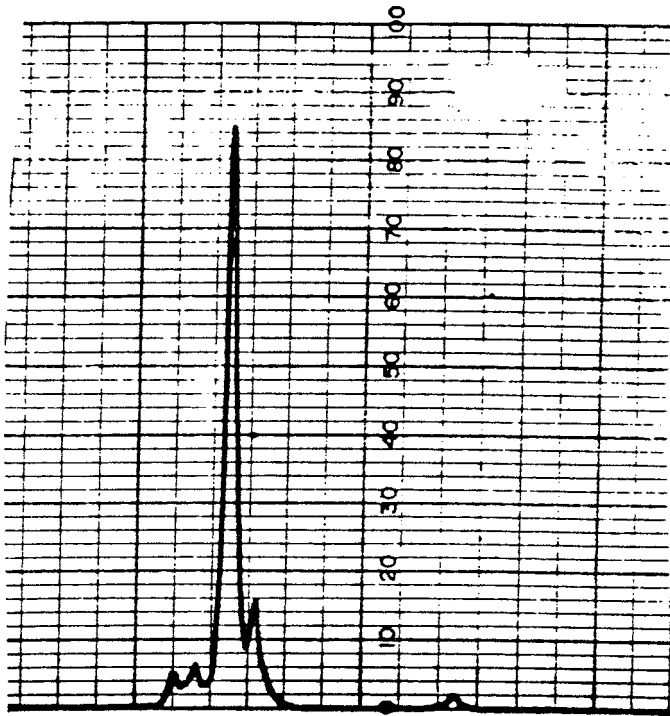


FIG. 4 Mercury Lamp Emission Spectrum Near 579 nm for Resolution Evaluation

less than 10 %. A double or triple monochromator should transmit efficiently over its entire spectral range. The couplings should be tested in at least two regions such as 459 cm⁻¹ for carbon tetrachloride and at 2855 cm⁻¹ for cyclohexane. Alternatively, sharp plasma lines from a low-pressure atomic source can be used. If intensity reductions are greater than

10 %, then the monochromator stages are out of alignment. Follow the manufacturer’s alignment procedures, or contact the manufacturer to restore coupling efficiency.

7.3.4 Stray Light Rejection, Grating Ghosts, and Laser Plasma Lines—A properly aligned spectrometer should be tested for rejection of stray light close to the laser frequency. Manufacturers specify stray light rejection in different ways and performance varies, so an empirical approach is best. One way that stray light can be measured is by scattering the laser off a sample of fine glass powder, such as that used in gas chromatography columns, and scanning from 10 to 50 cm⁻¹. Record the laser power and the photomultiplier dark signal at 25 cm⁻¹ with the slits closed; then measure the scattered light intensity with the slits open to a normal operating size (for example, 25- μ m width and 1-mm height), recording both slit height and width. If the stray light has increased since the previous measurement, contact the manufacturer for assistance. An alternate measurement of stray light can be performed using a powdered sample such as *L*-cystine (9 and 15 cm⁻¹ bands) measured against the Rayleigh scattering background as shown in Fig. 5.

7.3.4.1 To check for grating ghosts and laser plasma lines, scan through the entire spectral region (10 to 4000 cm⁻¹) under the same conditions used to measure stray light. Look for any sharp lines, which could be grating ghosts if ruled (not holographic) gratings are used, or they could be laser plasma emission lines incompletely filtered out.

7.3.5 Scanning—To check the scanning accuracy, a Raman spectrum for a test sample such as indene should be used. Band frequencies for indene are listed in Table 1. The measured values for the bands should deviate no more than 3 cm⁻¹ from the standard values given. Perform a frequency calibration if needed. The precision in a given spectral region should be checked by scanning over a major Raman band or an atomic

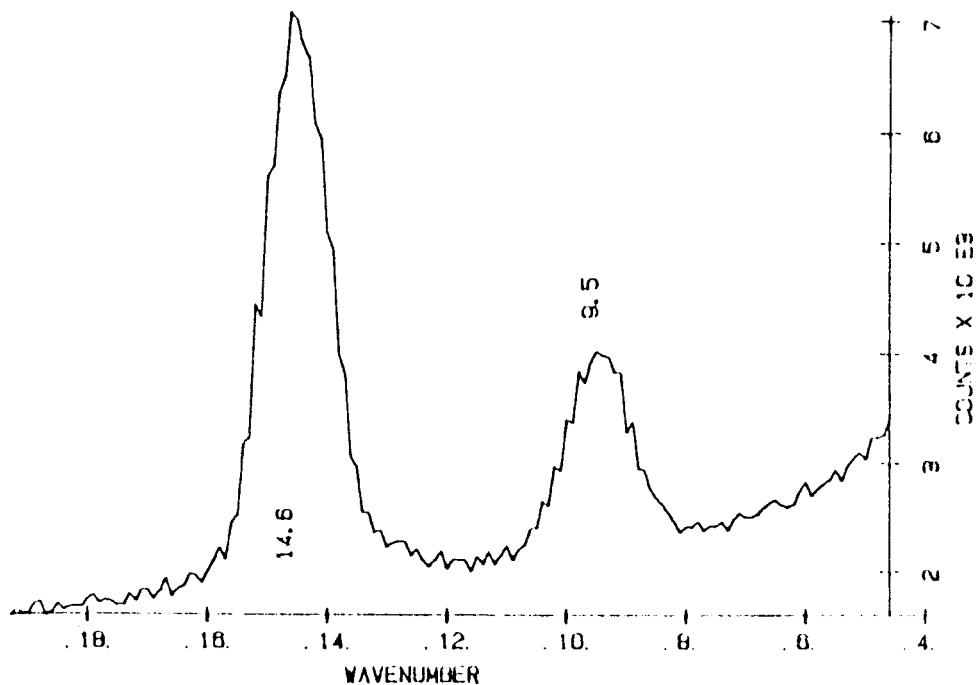


FIG. 5 *L*-cystine Raman Spectrum for Stray Light Measurement

emission line several times at different scan rates. Scan through the band, starting at a frequency at least 25 cm⁻¹ below it. For most instruments the band frequency should be reproducible to within 0.4 cm⁻¹, and the intensity reproducibility should be greater than 90 %.

7.4 Detector:

7.4.1 *Dark Signal Level*—The dark signal should be measured routinely with the slits closed and the room darkened. Photomultiplier tube failure is often signaled by excessive dark signal. A manufacturer's specification should not be used instead of empirical measurements. Exposing photomultiplier tubes to laser radiation should be avoided since irreversible damage may occur.

7.4.2 *Sensitivity*—If Raman signal intensity is reduced and it cannot be attributed to monochromator or sample alignment,

then the detector should be checked. The most common detector condition causing signal reduction is frost buildup on the window of the photomultiplier tube housing. The manufacturers of cooled housings suggest that they be shut down and dried out every six months. More frequent drying may be necessary if a housing is not sealed properly. Another way to improve sensitivity is to adjust the floating lens sometimes included in front of the photomultiplier tube. Adjusting this lens may expose a more responsive portion of the photocathode.

8. Keywords

8.1 Raman spectroscopy; scanning

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